NPAP-SOP-010
Date: May 15, 1998
Revision: 2
Reviewed:

NITRIC OXIDE (NO) AUDIT

by

Jack Bowen
J. Mark Holland
Andrew Reinhardt

ManTech Environmental Technology, Inc.
Research Triangle Park, NC

CAUTION

Disclaimer: This Standard Operating Procedure has been developed for use by ManTech Environmental Technology, Inc. in support of the National Performance Audit Program (NPAP) under contract to the U.S. Environmental Protection Agency and may not be applicable to the activities of other organizations.

Approved by:

Kenneth J. Caviston, Manager — Date
ManTech Environmental Technology, Inc.

Joe Elkins — Date
EPA NPAP Coordinator

Effective: When approved

CONTENTS

Page

Page

ATTACHMENT

"Section III. Gas Cylinder Regulator Equilibration" from *Field Instructions for the TECO 175 Multi-pollutant Audit Device*

FIGURES

1.0 SCOPE AND APPLICATION

This procedure covers the calibration of nitric oxide (NO) analyzers, and the certification of gas dilution audit devices used for the NO audit in the National Performance Audit Program (NPAP). The objective is to determine the operational status of gas dilution audit devices. This SOP addresses the NO analyzer calibration, audit device flow characterization and certification, and the Quick Check procedure.

2.0 SUMMARY AND PRINCIPAL

NO is audited with a gas dilution audit device of which there are two configurations currently in use, the gas dilution system (GDS) and the Thermo Environmental Inc. model 175 portable calibrator (175). These devices are assigned a pollutant gas cylinder with a certified NO concentration. The devices then undergo a flow characterization that consists of measuring the flows of pollutant gas and dilution (zero) air for each setting used in the field audits. The concentration of the cylinder is used with the audit device dilution ratios to determine the output concentration at each audit point.

The audit device is connected to a calibrated NO analyzer for verification of its output. For a detailed discussion of the operating principals of the NO analyzer, refer to the manufacturer's instruction manual. The NO analyzer readings for the high, medium, and low audit device outputs must compare to the calculated values within 3%, 5%, and 7%, respectively.

3.0 DEFINITIONS

MFC:	Mass Flow Controller
Working Standard:	Compressed gas cylinder which has been certified against a Standard Reference Material (SRM).
Lpm:	Liters per minute
ppb:	Parts per billion
Zero Air:	Ambient air scrubbed for O_3, sulfur, organic compounds, other reactive low molecular weight compounds, and moisture; CO converted to CO_2

4.0 SAFETY PRECAUTIONS

Observe standard safety precautions whenever electrical equipment is operated. The NO analyzer contains 120 volts AC, and the 175 contains 120 and 800 volts AC. Use normal precautions when working on the inside of the instruments with the power connected. Under no circumstance should the instruments be operated without an electrical ground. The instruments are supplied with a 3-wire, grounding line cord.

Always vent cylinders during purge cycles to a suitable outside vent. Place cylinders in approved racks to prevent them from falling.

5.0 FACILITIES REQUIREMENTS

This SOP requires a facility equipped with electricity, adequate bench space for the apparatus, and a continuous source of zero air for the NO analyzer, GDS, and the 175, as well as gas exhaust capabilities.

6.0 INTERFERENCES

- Contamination from leaks in the zero air system if the connecting tubing is not tightened properly or if the fittings are excessively worn.
- Small leaks in the regulator, not detected when the regulator is first attached to the cylinder.
- Electrical interferences
- Variable air flow
- Inefficient or exhausted air scrubbers
- Particulate matter in the air lines or capillaries

7.0 APPARATUS AND MATERIALS

- Electronic Manometer
- Mass Flow Controllers
- Temperature Sensor
- NIST traceable Mercury barometer
- NIST traceable NO gas cylinder with regulator

- Computer with laminar flow element (LFE) flow program installed
- Ambient level NO analyzer with 50 ppm range
- Bios® DryCal Flow Calibrator or LFEs, types 11, 5, and 3
- Zero air source
- Strip chart or VideoGraphic recorder
- Air pump, providing at least 5 Lpm
- 1/8" FEP Teflon® tubing
- 1/4" FEP Teflon® tubing
- 1/4" Brass or stainless steel tube fittings
- 1/8" Stainless steel tube fittings
- Mixing chamber
- Scrubber cartridges:
  - Purafil II®: to remove sulfur, organic compounds, and other reactive low molecular weight compounds
  - Silica gel: to remove moisture
  - Hopcalite®: to convert CO to CO_2 and remove O_3

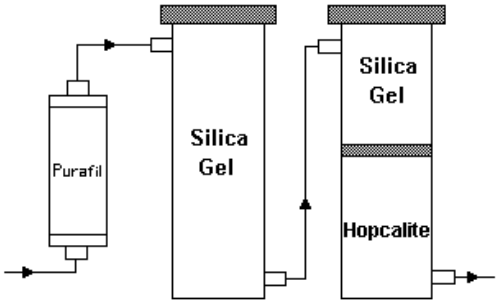

Figure 1.

Scrubber train

- Gas Dilution System, see Figure 2
- TECO Model 175, see Figure 3

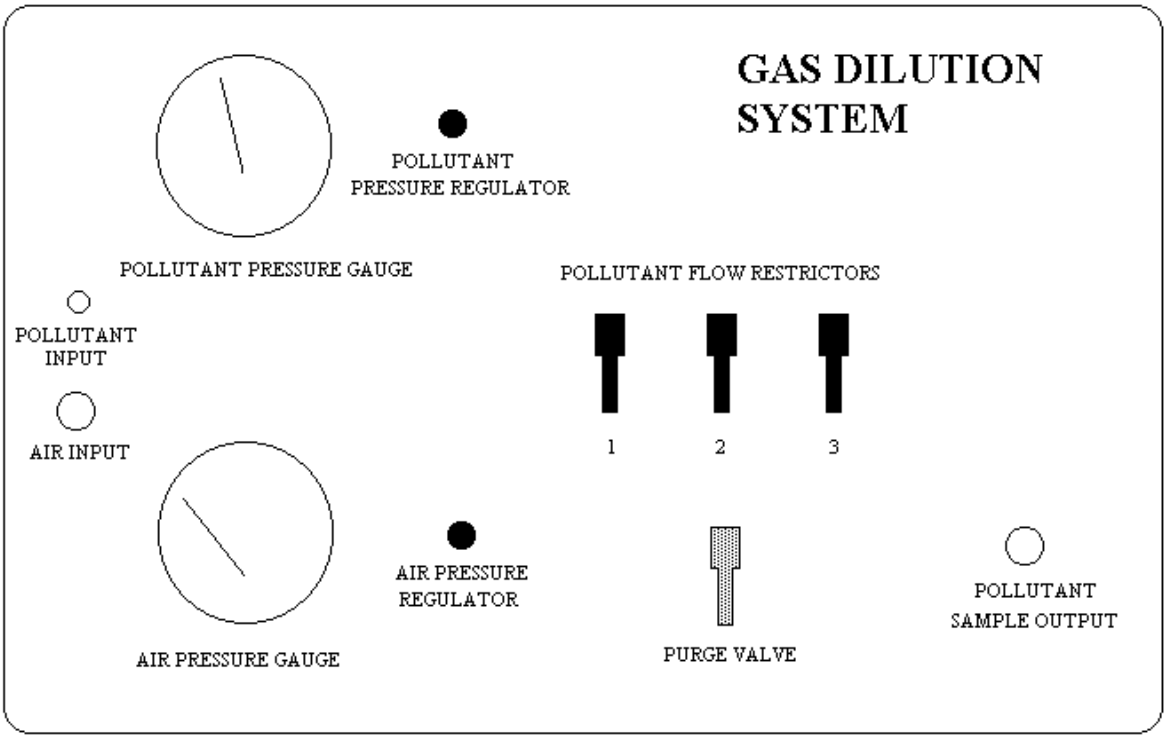

Figure 2. Front Panel Layout, Gas Dilution System

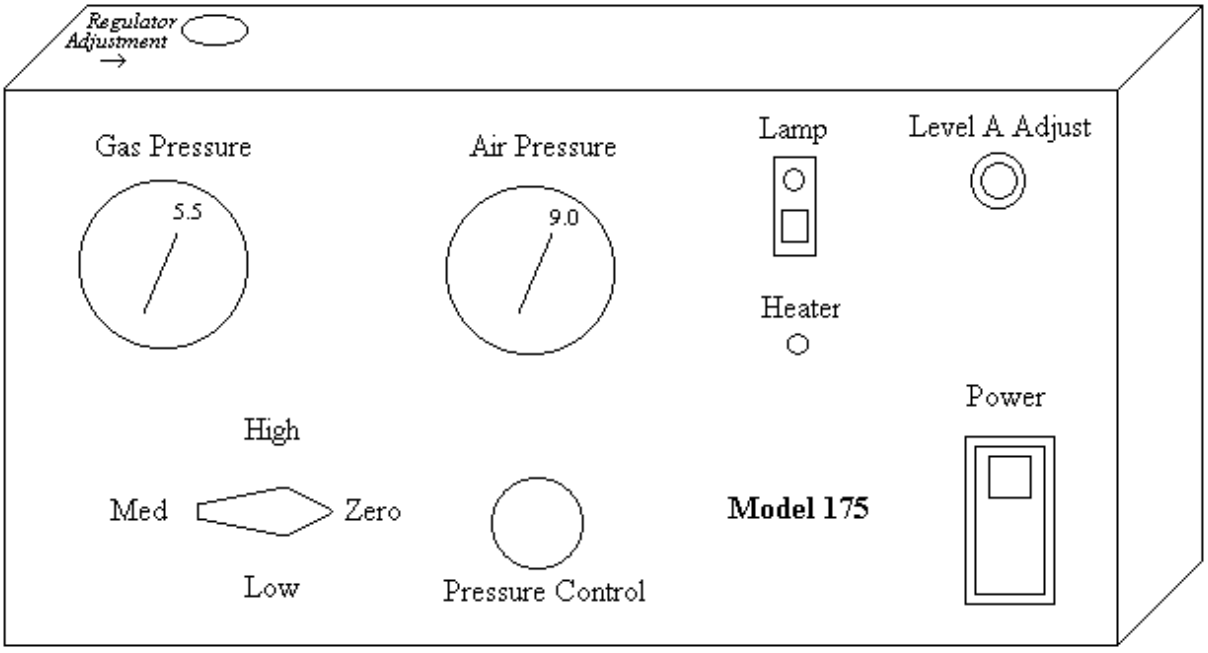

Figure 3. Front Panel Layout, Thermo Environmental Model 175

8.0 CALIBRATION AND ZERO/SPAN OF ANALYZER

8.1 Consult the NO instrument manual for proper operation and calibration procedures.

8.2 Perform a five-point calibration using NIST traceable gases on the analyzer every six months or after internal repairs. If problems occur, consult the manufacturer's manual for troubleshooting assistance.

8.3 Use a dilution system (MFCs and mixing chamber) to reduce the NIST traceable cylinder concentrations to levels usable by the analyzer.

- Adjust the dilution (zero) air MFC to obtain a dilution flow of 3 to 5 Lpm to the analyzer.
- Adjust the pollutant MFC to obtain the required flow for the desired calibration points.

8.4 <u>Calibration</u>

8.4.1 Using LFEs, electronic manometer, and the computer program "LFE Flow Calc" to determine flows.

1. Record the barometric pressure in the Zero/Span logbook.

2. Connect the dilution (zero) air line to a type 11 LFE for the dilution (zero) air flow measurement. Make sure that the zero air is on. Allow the pressure differential response on the electronic manometer to stabilize and record it, the LFE temperature, LFE serial number, and the MFC setting in the Zero/Span logbook. Reattach the dilution line to the mixing chamber.

3. Attach the pollutant line to a type 5 LFE. Turn on the pollutant flow. Allow the pressure differential response on the electronic manometer to stabilize and record it, the LFE temperature, LFE serial number, and the MFC setting in the Zero/Span logbook.

4. Access the "LFE Flow Calc" on the laboratory computer. Enter the flow data for both the zero and pollutant as requested by the program. Record the "LFE Input Flow at STP, cc min." in the Zero/Span logbook.

5. Calculate the dilution ratio using **Equation 1** in **Section 10.0 Calculations**. Record the dilution ration in the Zero/Span logbook.

6. Use **Equation 2** in **Section 10.0 Calculations** to determine the calculated output.

   Note: This first concentration level should be between 350 ppb and 450 ppb. If not, adjust the pollutant flow using the MFC to achieve this concentration and repeat **Steps 3 through 6**.

7. Remove the pollutant line from the LFE, attach it to the mixing chamber. Allow the analyzer to sample the NO gas until a stable reading is shown on the strip chart or VideoGraphic recorder. Record the instrument response in the Zero/Span logbook.

8. Determine the percent difference between the instrument response and the calculated concentration using **Equation 3** in **Section 10. Calculations**. Record the percent difference in the Zero/Span logbook.

   - Accept the point if the percent difference # ±1%. **Make no adjustments to the span potentiometer.**
   - If the percent difference is > ±1%, adjust the analyzer span potentiometer until agreement is reached. Always allow the analyzer to stabilize after an adjustment. **Make no further adjustments to the span pot during the remainder of this calibration.** Record the adjusted reading in the Zero/Span logbook.

9. Disconnect the pollutant line from the mixing chamber and reattach it to the type 5 LFE.

10. Repeat **Steps 3 through 8** for each of four upscale points, spaced evenly over the range of the analyzer. Obtain these points by adjusting the flows using the MFCs.

8.4.2 Using a DryCal to determine flows:

1. Dilution Flow

   A. Attach the line from the output of the dilution gas MFC to the input of the DryCal.
   B. Make sure that the zero air is on.
   C. Allow the DryCal to average 10 flows. Individual readings and the average are displayed on the front panel of the DryCal.
   D. Record the average dilution flow in the Zero/Span logbook.
   E. Reattach the dilution line to the mixing chamber.

2. Pollutant Flows

A. Attach the line from the output port of the pollutant MFC to the input of the DryCal.
B. Turn on the pollutant flow.
C. Allow the DryCal to average 10 flows. Individual readings and the average are displayed on the front panel of the DryCal.
D. Record the average pollutant flow in the Zero/Span logbook.
E. Calculate the dilution ratio using **Equation 1** in **Section 10.0 Calculations**. Record the dilution ratio in the Zero/Span logbook.
F. Use **Equation 2** in **Section 10.0 Calculations** to determine the calculated output.

Note: This concentration should be between 350 ppb and 450 ppb. If not, adjust the pollutant MFC to achieve this concentration and repeat **Steps C through E**.

G. Remove the pollutant line from the DryCal and attach it to the mixing chamber. Allow the analyzer to sample the NO gas until a stable reading is shown on the strip chart or VideoGraphic recorder. Record the instrument response in the Zero/Span logbook.

H. Use **Equation 4** in **Section 10.0 Calculations** to determine the percent difference between the instrument response and the calculated concentration. Record the percent difference in the Zero/Span logbook.
   - Accept the point if the percent difference # ±1% . **Make no adjustments to the span potentiometer.**
   - If the percent difference is >±1%, adjust the analyzer span potentiometer until agreement is reached. Always allow the analyzer to stabilize after an adjustment. **Make no further adjustments to the span pot during the remainder of this calibration**. Record the adjusted response in the Zero/Span logbook.

I. Disconnect the pollutant line from the mixing chamber and reattach it to the DryCal.
J. Repeat **Steps C-H** for each of four additional points which are evenly spaced over the range of the analyzer. Obtain these points by adjusting the flows using the MFCs.

8.5 Derive a calibration curve equation by plotting instrument response values (x) versus calculated concentration (y). See **Equation 4** in **Section 10.0 Calculations**. Use a least squares linear regression to determine the slope (m), y-intercept (b), and correlation (R^2) for this calibration.

1. Accept the calibration if:

   - The slope falls between 0.98 and 1.02.
   - The intercept lies between ±0.3.
   - Correlation $ 0.9999

2. Reject the calibration if the above criteria are not met. Consult the manufacturer's instrument manual for troubleshooting assistance.

8.6 **<u>Zero/Span</u>**

1. Perform an analysis for zero and an upscale response using an NIST traceable NO working standard prior to use.

2. Obtain the zero value while the analyzer is sampling house zero air. If the reading is not within ±0.2 ppb, adjust the analyzer's zero pot until the front panel reads zero.

3. Use either LFEs, electronic manometer, and the computer program "LFE Flow Calc" or the DryCal to determine flows.
   - Set the MFC to the span setting
   - Measure both the dilution and pollutant flows using either LFEs or a DryCal
   . Compute the dilution ratios using **Equation 1** in **Section 10.0** and the calculated concentration using **Equation 2** in **Section 10.0**.
   - Remove the line from the LFE, attach it to the glass mixing chamber. Allow the analyzer to sample the NO gas until a stable reading is shown on the strip chart or VideoGraphic recorder.
   - Record the front panel reading in the Zero/Span logbook.
   - Adjust the span value to meet specifications, if necessary. Record the adjusted value in the Zero/Span logbook.

4. Accept the check if the adjusted zero difference is within ±0.2 ppb and the adjusted span value is within ±2ppb of the calculated concentration (**See Equation 3**).

5. If the instrument cannot be adjusted within specifications, consult the manufacturer's instrument manual for troubleshooting assistance.

9.0 AUDIT DEVICES

9.1 Flow Characterization

1. To characterize the flows, measure the flows four times and average the results. The averaged flows are used to determine dilution ratios. If repairs that could affect the flows are made, check flows and compare the results to the full characterization. Recharacterize the flows if the percent difference > 2%.

2. Assign a certified audit cylinder, pump, and regulator to the TECO 175 or GDS.
   A. Maintain these assignments throughout the service life of the cylinder/equipment.

   B. Use the assigned pump, audit cylinder, and the regulator during the certification and verification procedures.

3. **175**: Plug the device into a stable 110 V power source and turn the power switch to the ON position. Warm-up the instrument until the heater indicator light comes on; this takes from 15 to 30 minutes. Set the UV lamp switch in the OFF position.

4. Use an NIST traceable flow measuring device to measure the pollutant flows at the **HIGH**, **MED**, and **LOW** settings, and the dilution flow at the **ZERO** setting. Connect a gas cylinder to the pollutant input port. Cap off the air input port. Cap off all but one of the output ports. Connect the remaining output port to the NIST traceable flow measuring device. Adjust flows as stated below:

CAUTION

To adjust the regulator on the device, reduce the pressure below the setting, and then adjust UP to the setting. DO NOT TAP the gauge. Recheck the gauge setting periodically and reset it if needed.

Cylinder regulator output pressure:

175: 15 psig
GDS: 45 psig

Device dilution (zero) air flow:

175: 9.0 psig
GDS: 18 psig

Device pollutant pressure gauge:

175: 5.5 psig
GDS: 26 psig

A. Using an LFE and electronic manometer to determine flows.

(1) Use a Type 3 for

175: HIGH
GDS: Valves 1 and 3 open, 2 closed

and

175: MED
GDS: Valves 2 and 3 open, 1 closed

(2) Use a Type 5 for

175: LOW setting.
GDS: Valve 2 open, Valves 1 and 3 closed

(3) Use a Type 11 for

175: ZERO setting (Dilution flow).
GDS: Valves 1, 2, and 3 closed

(4) Record the requested parameters on the "Dilution System Flow Certification Log."

(5) Access the "LFE Flow Calc" on the laboratory computer. Enter the data as requested by the program and record the "LFE Input Flow at STP, cc min." on the "Dilution System Flow Certification Log." These are the **certified flows**.

(6) **GDS**: Subtract the flow for valve 2 from the flow for valves 2 and 3 to obtain the flow for valve 3. This calculation is necessary since the flow for valve 3 is too low to be measured with the LFE.

B. Using a DryCal to determine flows.

(1) Allow the DryCal to average 10 flows. Individual readings and the average are displayed on the front panel of the DryCal. These are the **certified flows**.
(2) Record the requested parameters on the "Dilution System Flow Certification Form."

5. Use **Equation 1** in **Section 10.0 Calculations** to determine the dilution ratio for each setting.

6. For each setting, use the dilution ratio and the certified audit cylinder value for NO to determine the pollutant calculated concentration (**Equation 2** in **Section 10.0 Calculations**). Record the values in "Calc. Conc." on the form "System Certification Check for 175s and GDSs (Quick Check Form)."

9.2 Post-Audit Check Procedure

1. Remove the audit device and zero air system from the shipping container.

2. Remove the gas cylinder and regulator from their shipping container.

3. Replace the zero air scrubber materials as follows:
   A. Silica gel: when it turns pink or white
   B. Purafil II® chemisorbent media: when it turns brown or becomes saturated with moisture
   C. Hopcalite® Catalyst: when it has been in use for one year

9.2.1 Cylinder/Regulator Equilibration

> **CAUTION**
> This procedure must be performed in a well ventilated area or a vent line must be attached to the regulator outlet valve.

1. Follow **III. Gas Cylinder Regulator Equilibration** in the "Field Instructions for the TECO 175 Multi-pollutant Audit Device." (See Attachment)

2. Turn the cylinder regulator pressure adjustment clockwise to

   175: 15 psig
   GDS: 45 psig

3. Cap off the regulator outlet using a 1/8" stainless steel cap.

4. Open the regulator outlet valve and close the cylinder valve.

5. Observe the gauge pressures on the regulator.

   A. A regulator leak is indicated by a drop in pressure of more than 100 psi per hour:

      - Tighten fittings and repeat the purge procedure.
      - If the leak persists, replace the regulator and repeat the purge procedure.

B. A regulator allowing gas to leak from the first stage to the second stage is indicated by an increase greater than 10 psi per hour on the outlet pressure gauge:

- Replace the regulator.
- Repeat the regulator purge procedure.

CAUTION

Do not attempt to repair the regulator. It must be repaired by an authorized repair facility.

9.2.2 Audit Device Purge Cycle

1. Using 1/8" FEP Teflon® tubing, connect the regulator output to the audit device at the pollutant input port.

2. Attach a Swagelok® stainless steel cross fitting to the port labeled **OUTPUT**, located on the rear of the **175**. The **GDS** will already have this fitting attached. The cross allows you to connect two analyzers, simultaneously. If you are only connecting one analyzer, make sure the extra port is capped. Vent one port of the cross fitting to an exhaust.

3. Connect the **175** to a stable 110 volt power source. Turn the power switch ON. With the lamp switch in the OFF position, turn the Level A Adjust Potentiometer fully counter-clockwise to zero, see Figure 3. Allow the 175 to warm-up until the heater lamp is lit.

4. Open the cylinder regulator outlet valve and adjust the output pressure to

   175: 15 psig
   GDS: 45 psig

5. **175**: Set the selector valve in the HIGH position.
   GDS: Open valves 1, 2, and 3

6. Adjust the device pollutant pressure gauge to

   175: 5.5 psig
   GDS: 40 psig

   and purge the audit device for 15 minutes.

7. While the pollutant gas is purging, assemble the zero air system. Connect the zero air system to the air input port on the audit device.

8. When the 15 minute gas purge is completed, turn on the zero air.

9. Adjust the device zero air

   175: 9.0 psig
   GDS: 18 psig

10. Recheck the gauge setting periodically and reset it if needed.

11. **175**: Check that pollutant pressure is at 5.5 psig.
    GDS: Reduce the pollutant pressure to 26 psig on a GDS, and close valve 2.

    Recheck the gauge setting periodically and reset it if needed.

12. Allow the audit device to purge for an additional 5 minutes.

13. Connect the analyzer's sample port to the audit device.

9.2.3 Audit Device Certification

1. Allow the analyzer to sample the high concentration gas mixture until a stable trace is observed. If a stable trace is not indicated after 15 minutes, disconnect the analyzer's sample line from the audit device and repeat the regulator equilibration procedure. See Attachment.

2. After stabilization, record the analyzer's front panel response on the form "System Certification Check For 175s And GDSs (Quick Check)."

3. Run the remaining concentrations in the order given for each device:

   175: MED
   LOW
   ZERO

   GDS: Valves 2 and 3 open, valve 1 closed
   Valve 3 open, valves 1 and 2 closed.
   Valves 1, 2, and 3 closed

   Record the analyzer responses on the form "System Certification Check For 175s And GDSs (Quick Check)."

4. For each point, calculate the percent differences between the analyzer readings and the calculated concentrations using **Equation 3** in **Section 10.0 Calculations**. Record these values on the "System Certification Check For 175s And GDSs (Quick Check)."

5. Accept the Quick Check if the following criteria are met:

175	GDS	Difference
High	Valves 1,3	±3%
Med	Valves 2,3	±5%
Low	Valve 3	±7%
Zero	Valves Closed	±0.2 ppb

   If the criteria are not met, attempt to determine the cause and repair it. If the cause is not determined, send the device to Repair.

6. Disconnect the sample line from the analyzer.

7. Shut off the regulator outlet valve on the gas cylinder.

8. Disconnect the 1/8" Teflon® tubing at the regulator. Record the cylinder pressure on the "System Certification Check For 175s And GDSs (Quick Check)."

9. Close the cylinder valve.

10. Bleed the regulator and bring all gauge needles to zero.

11. Disconnect all tubing and place it inside a plastic storage bag.

12. Remove the regulator from the cylinder and cap the regulator inlet and outlet fittings.

10.0 CALCULATIONS

Equation 1:

$$\frac{\text{Gas Flow}}{\text{(Gas Flow + Zero Air Flow)}} = \text{Dilution Ratio}$$

Equation 2:

Dilution Ratio x Cylinder Concentration = Calculated Concentration

Equation 3:

$$\frac{\text{Instrument Response - Calc. Concentration}}{\text{Calc. Concentration}} \times 100 = \text{Percent Difference}$$

Equation 4:

$$y = mx + b$$

where x = instrument response values
y = calculated concentration
m = slope
b = y-intercept

11.0 QUALITY ASSURANCE/QUALITY CONTROL

11.1 Quality Control Checks

PROCEDURE	ACCEPTANCE CRITERIA	
Regulator Check	No leaks from regulator or between regulator stages.	
Pump Check	Flow through zero air system at 18 psi $\geq$ 5 Lpm	
Quick Check	High / Valves 1&3 Med / Valves 2&3 Low / Valve 3 Zero	± 3% of the calculated value ± 5% of the calculated value ± 7% of the calculated value ± 0.2 ppb
Flow Check	±2% of the certified value	
Cylinder Recertification	± 3% of the certified value	

11.2 Quality Controls

An overall procedural control is the multi-point calibration of the NO analyzer. Other QC include the zero and span checks and control charts. The EPA also conducts performance and systems audits.

Anytime data exceeds the QC criteria or there is an indication of change in the performance of a dilution system or its components, a careful inspection is made of the complete system. If questions remain on the reliability of the system, it is not shipped to any participants until all problems are resolved.

12.0 LEAK CHECK

12.1 175 Leak Check

1. Cap off the gas port and the output port.

2. Pressurize the zero air port to 12 psi.

3. Use a liquid leak detector to check all connections and fittings.

4. Cap the zero air port and pressurize the gas port to 8 psi, and repeat the leak check.

12.2 GDS Leak Check

1. Remove the four screws that secure the dilution system to the metal suitcase.

2. Cap the air input and the output port(s).

3. Connect house zero air (preset at 50 psi) to the pollutant input port and adjust the pollutant pressure regulator until the pollutant pressure gauge reads 26 psi.

4. Open all three toggle valves.

5. Set the dilution system in the case so that all the fittings and tubing underneath are accessible.

6. Use a liquid leak detector to check all connections from the pollutant input to the pollutant sample output.

7. Switch the house zero air to the air input port and cap the pollutant input port.

8. Adjust the air pressure regulator until the air pressure gauge reads 18 psi.

9. Use the liquid leak detector to check all connections from the air input to the mixing chamber.

10. Tighten or replace any leaking or broken fittings or tubing.

11. Secure the dilution system in the suitcase with the four screws.

13.0 SHIPPING

1. After all checks have been performed on the device, check the audit kit for completeness of parts.

2. Check the audit cylinder pressure.

3. Select the next participant from the audit list.

4. Record the audit device number being sent to the participant.

5. Prepare a data packet with the following:

   - Cover letter
   - Instructions for conducting the audit
   - Data sheets
   - Return instructions with return address labels and associated paperwork
   - Data return envelope
   - Questionnaire

6. Enclose the packet in the shipping box with the audit kit.

7. Place the participant address label on the shipping box.

8. Ship using the appropriate carrier, following the appropriate 49CFR regulations.

9. Enter the shipment into the NPAP database.

14.0 DATA REPORTING

Audit data is sent directly to the Data Entry personnel and handled according to **NPAP-SOP-005: Computer Data Entry, Report Printing, and System Maintenance for the NPAP**.

15.0 REFERENCES

Thermo Environmental, Model 42, Chemiluminescence NO-NO_2-NO_x Analyzer Instruction Manual, Thermo Environmental Instruments Inc.

Thermo Environmental, Model 42B/E, Chemiluminescence NO-NO_2-NO_x Analyzer Instruction Manual, Thermo Environmental Instruments Inc.

ATTACHMENT

"Section III. Gas Cylinder Regulator Equilibration" from *Field Instructions for the TECO 175 Multi-pollutant Audit Device*